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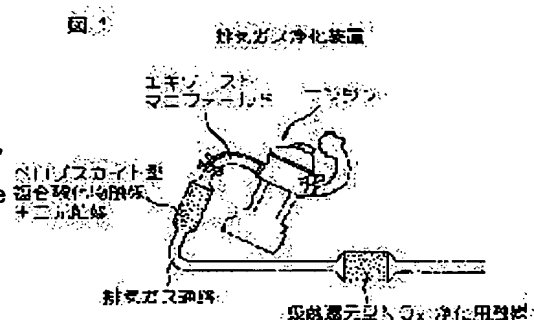
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(54) APPARATUS FOR CLEANING EXHAUST GAS FROM INTERNAL COMBUSTION ENGINE AND CATALYST FOR CLEANING EXHAUST GAS**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide an apparatus for cleaning an exhaust gas in which the temperature range to clean NO_x is enlarged.

SOLUTION: In the apparatus for cleaning the exhaust gas, a catalyst prepared by supporting a noble metal on a perovskite type double oxide containing at least 2 kinds of metals is arranged on the upstream side of an exhaust gas passage of a lean burn engine and another catalyst for cleaning NO_x is arranged on the downstream side of the catalyst. The perovskite type double oxide is expressed by a chemical formula, $A_{1-x}A'_xM_{1-y}Ti_yO_3$ (A represents at least one metal of La, Nd, Sm and Gd, A' represents at least one metal of K, Rb and Cs, M represents at least one metal of Mn, Co, Fe and Ni, and (x) and (y) satisfy respectively $0 < x < 1$ and $0 < y < 1$. More preferably, A' represents Rb.

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CLAIMS

[Claim(s)]

[Claim 1] The exhaust gas purge characterized by having arranged the catalyst which supported noble metals to the perovskite mold multiple oxide which contains at least two sorts of metals in the upstream of the exhaust gas path of a lean burn engine, and having arranged the catalyst which purifies NO_x to the downstream of said catalyst.

[Claim 2] To the upstream of the exhaust gas path of a lean burn engine, it is chemical formula: $A_{1-x}A'_xM_{1-y}Ti_yO_3$ (A). At least one sort of La, Nd, Sm, and Gd and A' At least one sort of K, Rb, and Cs and M The exhaust gas purge characterized by having arranged the catalyst which supported noble metals to the perovskite mold multiple oxide expressed with at least one sort of Mn, Co, Fe, and nickel, $0 < x < 1$, and $0 < y < 1$, and having arranged the catalyst which purifies NO_x to the downstream of said catalyst.

[Claim 3] Chemical formula: The catalyst for exhaust gas purification characterized by noble metals being supported by the perovskite mold multiple oxide expressed with $A_{1-x}Rb_xM_{1-y}Ti_yO_3$ (A is at least one sort of La, Nd, Sm, and Gd, and M is at least one sort of Mn, Co, Fe, and nickel, $0 < x < 1$, and $0 < y < 1$).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the exhaust gas purge to which the temperature requirement which can purify NOx was expanded in more detail about the equipment for purifying the exhaust gas discharged by internal combustion engines, such as car motor.

[0002]

[Description of the Prior Art] In recent years, it has been a global technical problem for environmental protection to stop the total amount of the carbon dioxide (CO₂) discharged by internal combustion engines, such as car motor, and to stop the yield of nitrogen oxides (NO_x). As this countermeasure, the lean burn engine was developed for the purpose of the improvement in fuel consumption, the catalyst for occlusion reduction type NO_x purification to which the function which carries out occlusion of NO_x to the conventional three way component catalyst by lean atmosphere was made to add in order to purify that exhaust gas was developed, and a fixed success is stored to the above-mentioned technical problem.

[0003] as for this lean burn engine, an air-fuel ratio (A/F) always burns a fuel under Lean's (air is superfluous) conditions — making — temporary — SUTOIKI(theoretical air fuel ratio) — it is made to burn under conditions [being rich (a fuel being superfluous)] Combustion removal of the hydrocarbon (HC) and carbon monoxide (CO) in exhaust gas is efficiently carried out by operation of an oxidizing atmosphere and a catalyst by the Lean side, on the other hand, by the Lean side, it is caught by occlusion material, it is emitted to the bottom of temporary SUTOIKI — a rich condition, and reduction purification of NO_x is carried out by operation of the temporary reducing atmosphere and catalyst.

[0004] Conventionally, alkali metal or alkaline earth metal is used, the salt of catalyst components, such as platinum, and NO_x occlusion material is ****(ed) to ****, such as gamma-alumina, and the catalyst for exhaust gas purification is constituted by the NO_x occlusion material of this catalyst for occlusion reduction type NO_x purification. Such a catalyst for exhaust gas purification is indicated by JP,9-248458,A, JP,10-33984,A, and JP,10-128114,A.

[0005] On the other hand, the catalyst for NO_x catalytic reduction which it is known that a specific perovskite mold multiple oxide has the operation which decomposes NO_x into N₂ and O₂, for example, ****(ed) the specific perovskite mold multiple oxide to JP,5-261289,A, JP,5-245372,A, and JP,6-315634,A at **** is indicated.

[0006]

[Problem(s) to be Solved by the Invention] However, with the catalyst for occlusion reduction type NO_x purification which ****(ed) alkali metal or alkaline earth metal, the NO_x purification engine performance of whenever [catalyst temperature / exceeding about 500 degrees C] needed to be raised. Moreover, the NO_x purification engine performance under the conditions that exhaust gas temperature like [at the time of engine starting] is low needed to be raised.

[0007] Moreover, although the combustion under temporary SUTOIKI for returning NO_x introduced into a catalyst — rich conditions is needed by the method which purifies NO_x by this occlusion reduction, such combustion uses some fuels and is made to generate it by making a part of fuel consumption into a sacrifice. For this reason, in order to raise fuel consumption further, to lessen the frequency of the combustion under temporary SUTOIKI — rich conditions as much as possible is desired. On the other hand, the catalyst containing the conventional perovskite mold multiple oxide needed to raise the NO_x purification engine performance, in order to use it for purification of the exhaust gas discharged by internal combustion engines, such as car motor.

[0008] Therefore, this invention is divided and aims at offering the exhaust gas purge to which the temperature requirement which can purify NO_x can be made to expand conventionally.

[0009]

[Means for Solving the Problem] The above-mentioned purpose is attained by the exhaust gas purge

characterized by having arranged the catalyst which supported noble metals to the perovskite mold multiple oxide which contains at least two sorts of metals in the upstream of the exhaust gas path of a lean burn engine, and having arranged the catalyst which purifies NOx to the downstream of this catalyst.

[0010] That is, this invention is an exhaust gas purge with which noble metals, such as platinum, have arranged the catalyst (a "perovskite mold multiple oxide catalyst" is called hereafter.) which comes to carry out direct **** to the upstream of an exhaust gas path, and the catalyst for NOx purification has been arranged on a specific perovskite mold multiple oxide at the downstream. The reason the above-mentioned purpose is attained by the exhaust gas purge of this configuration is considered as follows.

[0011] By the difference of the atomic radius of the metallic element in which the perovskite mold multiple oxide containing at least two sorts of metallic elements is generally contained, a strain arises and gets down to a crystal and it is thought that this crystal strain does a certain activity operation at NOx, and acts in [this activity operation and operation of catalyst components, such as platinum,] multiplication. And this multiplication-operation becomes remarkable by direct **** of the catalyst components, such as platinum, being carried out on a perovskite mold multiple oxide, and it is thought that the operation which decomposes NOx into N2 and O2 is raised.

[0012] Here, it became clear that a specific perovskite mold multiple oxide catalyst can maintain the operation to which exhaust gas temperature has sufficient endurance, and carries out decomposition purification of NOx also under the conditions exceeding 1000 degrees C. For this reason, such a perovskite mold multiple oxide catalyst is added to the usual catalyst for NOx purification, is arranged in the location near the engine combustion chamber of the upstream, and can be used as a catalyst for which temperature purifies NOx in exhaust gas under high conditions. The NOx purification engine performance can be raised as the whole exhaust gas purge by the upper limit temperature which can purify NOx is not only raising by that cause, but the load with which the catalyst for NOx purification of the downstream purifies NOx being mitigated.

[0013] Moreover, if the catalyst for NOx purification of this downstream is a catalyst for occlusion reduction type NOx purification, from the amount of NOx by which occlusion is carried out being reduced, the frequency of the combustion under temporary SUTOIKI - rich conditions can be lessened, and improvement in fuel consumption can be brought about. Moreover, the perovskite mold multiple oxide catalyst of the upstream is arranged in the location near an engine combustion chamber, and as compared with the catalyst for NOx purification of the downstream, whenever [catalyst temperature] can become high quickly at the time of engine starting, and, for this reason, it can also enable purification at an early stage of NOx.

[0014] Moreover, in addition to these perovskite mold multiple oxide catalysts and the catalyst for NOx purification, the exhaust gas purge of this invention can be equipped with the three way component catalyst which supported noble metals etc. to metallic-oxide support like gamma-alumina. The higher purification engine performance also about HC and CO can be obtained by this, if a perovskite mold multiple oxide catalyst and a three way component catalyst are made to live together, when whenever [catalyst floor temperature] goes up by the catalytic activity of a three way component catalyst, the NOx purification engine performance of a perovskite mold multiple oxide catalyst will improve, and the load which purifies NOx of the catalyst for NOx purification of the downstream will be mitigated further.

[0015]

[Embodiment of the Invention] The perovskite mold multiple oxide catalyst which supported noble metals to the perovskite mold multiple oxide which contains at least two sorts of metals in the upstream of the exhaust gas path of a lean burn engine is arranged, the catalyst for NOx purification is arranged and the exhaust gas purge of this invention is constituted by the downstream of this catalyst. The injection type jump-spark-ignition internal combustion engine in a cylinder which gaseous mixture [Lean / as the whole inside of a gas column] is burned, and realizes stratification combustion is illustrated by this lean burn engine, and a diesel type internal combustion engine is also contained in it. Since these internal combustion engines burn a fuel under the Lean conditions, NOx occurs comparatively so much, and purification of NOx is needed.

[0016] A perovskite mold multiple oxide comes to contain at least two sorts of metallic elements. A metallic element can be chosen from s-block metallic element, d-block metallic element, p-block metallic element, and f-block metallic element as arbitration here. Specifically Sodium (Na), a potassium (K), a rubidium (Rb), caesium (Cs), Calcium (calcium), barium (Ba), strontium (Sr), A lanthanum (La), an yttrium (Y), a cerium (Ce), PURASEOJIUMU (Pr), Neodymium (Nd), samarium (Sm), a europium (Eu), a gadolinium (Gd), Titanium (Ti), tin (Sn), a zirconium (Zr), manganese (Mn), They can be iron (Fe), cobalt (Co), nickel (nickel), chromium (Cr), niobium (Nb), copper (Cu), vanadium (V), molybdenum (Mo), a tungsten (W), zinc (Zn), a tantalum (Ta), etc.

[0017] In a desirable mode a perovskite mold multiple oxide $A_{1-x}A'_xM_{1-y}Ti_yO_3$ (at least one sort of La, Nd, Sm, and Gd and A' A) At least one sort of K, Rb, and Cs and M It is a specific perovskite mold multiple oxide containing Ti which has at least one sort of chemical formulas of Mn, Co, Fe, and nickel. $0 < x < 1$ -- it is -- more

-- desirable -- $0.05 < x < 0.45$ -- further -- desirable -- $0.2 < x < 0.4$ -- it is -- $0 < y < 1$ -- it is -- more -- desirable -- $0.05 < y < 0.45$ -- it is $0.2 < y < 0.4$ still more preferably.

[0018] More preferably a perovskite mold multiple oxide $A_{1-x}Rb_xM_{1-y}Ti_yO_3$ (at least one sort of La, Nd, Sm, and Gd and M A) It is a specific perovskite mold multiple oxide containing Rb and Ti which have at least one sort of chemical formulas of Mn, Co, Fe, and nickel. $0 < x < 1$ -- it is -- more -- desirable -- $0.05 < x < 0.45$ -- further -- desirable -- $0.2 < x < 0.4$ -- it is -- $0 < y < 1$ -- it is -- more -- desirable -- $0.05 < y < 0.45$ -- it is $0.2 < y < 0.4$ still more preferably.

[0019] The perovskite mold multiple oxide catalyst with which noble metals were supported by such specific perovskite mold multiple oxide being able to offer the higher NO_x purification engine performance under an elevated temperature, and excelling also in endurance is found out. This reason is guessed as follows, although it is not necessarily clear.

[0020] In addition to the strain of the crystal by the difference of an above-mentioned atomic radius, the crystal structure becomes instability more, an oxygen atom produces valence change, and the perovskite mold multiple oxide which has the above chemical formulas is considered because absorption/emission of the oxygen can be carried out, in order for a specific element to permute a part of the crystal lattice. Moreover, in the perovskite mold multiple oxide of this structure, the element of B site can do a oxidation reduction operation so, this oxidation reduction operation is divided, and when some elements of B site are permuted by titanium, what becomes remarkable is presumed.

[0021] Moreover, the following thing is considered as a reason. In the catalyst for occlusion reduction type NO_x purification by which a conventional alkali metal or alkaline earth metal was ****(ed), it is thought that alkali metal or alkaline earth metal changes to a nitrate under the Lean conditions, and changes to a carbonate under rich conditions. At the temperature exceeding about 500 degrees C, decomposition arises and, for this reason, these salts are considered that the NO_x occlusion engine performance in an elevated temperature falls.

[0022] On the other hand, while the above-mentioned perovskite mold multiple oxide is stabilized by the compound effectiveness also under an elevated temperature, it is presumed to be that to which some of potassiums of A site, rubidiums, or caesium [at least] can be isolated from a perovskite mold multiple oxide, the anion which remains acts on as a base point to NO_x, and the potassium of a cation, a rubidium, or caesium captures anion-ized NO_x under an elevated temperature. Moreover, a rubidium has a property unstable especially and is presumed for the property to bring about such capture of NO_x effectively.

[0023] Thus, an operation of the oxygen absorption/emission etc. can act in multiplication with the catalysis of noble metals, the above-mentioned specific perovskite mold multiple oxide can function as NO_x occlusion material under an elevated temperature further, and what offers the high NO_x purification engine performance under an elevated temperature by it is presumed.

[0024] Preparation of such a perovskite mold multiple oxide can be performed by making it a water solution, and heating at 400-1000 degrees C in air, after drying, mixing and, after, mixing powder, such as a nitrate of the element contained, acetate, and a chloride, at a predetermined rate for example.

[0025] Platinum (Pt), palladium (Pd), a rhodium (Rh), gold (Au), silver (Ag), and the noble metals chosen from at least one sort of iridium (Ir) are supported by such perovskite mold multiple oxide, and a perovskite mold multiple oxide catalyst is prepared. This **** was chosen from the approach of the arbitration which can make metal particles support on support, for example, can be performed by the depositing method, the adsorption process, the ion-exchange method, the reduction depositing method, an evaporation-to-dryness method, etc.

[0026] 0.1-5g of these noble metals is more preferably supported with an amount (0.3-4g) on the basis of the mass of 100g of a perovskite mold multiple oxide. Preferably, noble metals are supported after grinding etc. adjusts a perovskite mold multiple oxide to the particle size of 0.05-20 micrometers. It is for making homogeneity distribute noble metals by the perovskite mold multiple oxide top.

[0027] The catalyst for NO_x purification arranged at the downstream of a perovskite mold multiple oxide catalyst can be a catalyst of the arbitration which can purify NO_x, for example, can be a catalyst for occlusion reduction type NO_x purification with which catalyst components, such as NO_x occlusion material, such as alkali metal or alkaline earth metal, and platinum, were ****(ed) by ****, such as gamma-alumina. Moreover, this catalyst for NO_x purification can also be adsorption material like the zeolite which adsorbs or absorbs NO_x temporarily or in the long run by the base point or pore, the alkali matter, and various multiple oxides, or an absorber.

[0028] Moreover, in addition to these perovskite mold multiple oxide catalysts and the catalyst for NO_x purification, the exhaust gas purge of this invention can be equipped with the three way component catalyst with which noble metals were supported by metallic-oxide support like gamma-alumina. This three way component catalyst coexists with a perovskite mold multiple oxide catalyst, and can be arranged, or can be arranged at the downstream of a perovskite mold multiple oxide catalyst.

[0029] Although these perovskite mold multiple oxide catalysts, the catalyst for NO_x purification, and a three

way component catalyst can be made into the catalyst which has an exhaust gas path by carrying out a coat to the usual monolith support of a honeycomb configuration with a wash coat etc., they can constitute the exhaust gas purge of this invention also from carrying out a direct coat to the wall of an exhaust pipe.

[0030] Drawing 1 -2 illustrate the configuration of the exhaust gas purge of this invention typically, and drawing 1 is an example by which the catalyst for occlusion reduction type NOx purification has been arranged at the lower stream of a river by arranging a perovskite mold multiple oxide catalyst and a three way component catalyst together at the exhaust pipe of the lower stream of a river of an engine combustion chamber. Drawing 2 is an example by which the perovskite mold multiple oxide catalyst has been arranged at the exhaust manifold of an engine combustion chamber outlet, and the three way component catalyst and the catalyst for occlusion reduction type NOx purification have been arranged on the lower stream of a river. Hereafter, an example explains this invention more concretely.

[0031]

[Example] Examples 1-4 illustrate the exhaust gas purge of the configuration of drawing 1, examples 5-8 illustrate the exhaust gas purge of the configuration of drawing 2, and examples 9-12 illustrate the perovskite mold multiple oxide catalyst which is excellent in the NOx purification engine performance in an elevated temperature.

[0032] It is the following, and an example 1 perovskite mold multiple oxide catalyst and the 1st catalyst which consists of a three way component catalyst were made and prepared. Mn(NO₃) 2.6H₂O (780g Sm(NO₃) 3.6H₂O and 76g) of KNO₃, 504g, And after dissolving and stirring the titania sol containing 60g of solid content at 3000 cc ion exchange water, Moisture was evaporated, desiccation of 120 degree-Cx 2 hours and temporary quenching of 480 degree-Cx 5 hours were performed, subsequently baking of 850 degree-Cx 10 hours was performed, and the powder of perovskite mold multiple oxide Sm_{0.7}K_{0.3}Mn_{0.7}Ti_{0.3}O₃ was obtained. After having made 2000 cc ion exchange water distribute 500g of this obtained multiple oxide powder, stirring and adding a dinitrodiammine platinum nitric-acid water solution by 20gPt considerable amount, moisture was evaporated, desiccation of 120 degree-Cx 2 hours and baking of 500 degree-Cx 2 hours were performed, and Pt support perovskite mold multiple oxide powder was obtained.

[0033] Next, to this Pt support perovskite mold multiple oxide powder, 250g gamma-alumina powder was mixed, the ion exchange water of the alumina sol which corresponds on the basis of the total solid content at solid content 20 mass %, and optimum dose was added and stirred, and the slurry was prepared. After making 210 g quart of this slurry monolith support with a diameter [of 93mm] x die length of 100mm as solid content and performing desiccation of 120 degree-Cx 2 hours, and baking of 500 degree-Cx 2 hours, using the palladium nitrate water solution of a 3.5gPd considerable amount, palladium was further supported by the ion-exchange method, and the 1st catalyst was acquired.

[0034] It is the following, and the 2nd catalyst which consists of a catalyst for occlusion reduction type NOx purification was made and prepared. To 300g gamma-alumina powder and 300g titania powder, the ion exchange water of the alumina sol which is equivalent to solid content 30 mass % on the basis of the total solid content with these powder, and optimum dose was added and stirred, and the slurry was prepared. 260 g quart of this slurry was made monolith support with a diameter [of 103mm] x die length of 155mm as solid content, and desiccation of 120 degree-Cx 2 hours and baking of 500 degree-Cx 2 hours were performed.

[0035] Next, after dipping this monolith support by which the coat was carried out in the dinitrodiammine platinum nitric-acid water solution of 3gPt considerable amount, and the water solution which dissolved the nitric-acid rhodium of a 0.65gRh considerable amount in 2000 cc ion exchange water and stirring for 2 hours, desiccation of 120 degree-Cx 2 hours and baking of 300 degree-Cx 1 hour were performed. Next, 0.26 mols barium acetate and a 0.13-mol acetic-acid lithium were supported by the sinking-in method to the monolith support with which this Pt and Rh were supported, finally it calcinated at 500 degrees C to it, and the 2nd catalyst was acquired to it. The 1st catalyst and the 2nd catalyst which were acquired have been arranged on the lower stream of a river of an engine combustion chamber like drawing 1, and the exhaust gas purge of this invention was constituted.

[0036] The powder of perovskite mold multiple oxide La_{0.7}K_{0.3}Mn_{0.7}Ti_{0.3}O₃ was obtained like the example 1 except having replaced with Sm(NO₃) of 2780g of examples 3.6H₂O, and having used 760g La(NO₃) 3.6H₂O. The exhaust gas purge of this invention was constituted combining the 2nd catalyst which prepared the 1st catalyst like the example 1 and was prepared like the example 1 except having used 500g of this powder.

[0037] The powder of perovskite mold multiple oxide Nd_{0.7}K_{0.3}Mn_{0.7}Ti_{0.3}O₃ was obtained like the example 1 except having replaced with Sm(NO₃) of 3780g of examples 3.6H₂O, and having used 770g Nd(NO₃) 3.6H₂O. The exhaust gas purge of this invention was constituted combining the 2nd catalyst which prepared the 1st catalyst like the example 1 and was prepared like the example 1 except having used 500g of this powder.

[0038] The powder of perovskite mold multiple oxide Nd_{0.7}Rb_{0.3}Mn_{0.7}Ti_{0.3}O₃ was obtained like the example 3

except having replaced with KNO_3 of 476g of examples, and having used 111g RbNO_3 . The exhaust gas purge of this invention was constituted combining the 2nd catalyst which prepared the 1st catalyst like the example 1 and was prepared like the example 1 except having used 500g of this powder.

[0039] Except not using the powder of an example of comparison 1 perovskite mold multiple oxide, like the example 1, the coat of the 70g gamma-alumina was carried out to monolith support with a diameter [of 93mm] x die length of 100mm, next palladium was further supported using the palladium nitrate water solution of a 3.5gPd considerable amount, and the 1st catalyst was prepared. The exhaust gas purge for a comparison was constituted combining this 1st catalyst, and an example 1 and the 2nd catalyst prepared similarly.

[0040] It is the following, and the 1st catalyst which consists of an example 5 perovskite mold multiple oxide catalyst was made and prepared. Like the example 1, the powder of perovskite mold multiple oxide $\text{Sm}_{0.7}\text{K}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ was created, and 20g Pt was supported like the example 1 to 500g of this powder. To the powder of obtained Pt support perovskite mold multiple oxide, the ion exchange water of the alumina sol which is equivalent to solid content 30 mass % on the basis of the total solid content, and optimum dose was added and stirred, and the slurry was prepared. 100 g quart of this slurry was made monolith support with a diameter [of 80mm] x die length of 95mm as solid content, desiccation of 120 degree-Cx 2 hours and baking of 500 degree-Cx 1 hour were performed, and the 1st catalyst was acquired.

[0041] It is the following, and the 2nd catalyst which consists of a three way component catalyst was made and prepared. To gamma-alumina powder, the ion exchange water of the alumina sol which is equivalent to solid content 20 mass % on the basis of the total solid content with this powder, and optimum dose was added and stirred, and the slurry was prepared. After making 210 g quart of this slurry monolith support with a diameter [of 93mm] x die length of 100mm as solid content and performing desiccation of 120 degree-Cx 2 hours, and baking of 500 degree-Cx 2 hours, using the palladium nitrate water solution of a 3.5gPd considerable amount, palladium was supported by the ion-exchange method and the 2nd catalyst was acquired.

[0042] It is the following, and the 3rd catalyst which consists of a catalyst for occlusion reduction type NO_x purification was made and prepared. To 300g gamma-alumina powder and 300g titania powder, the ion exchange water of the alumina sol which is equivalent to solid content 30 mass % on the basis of the total solid content with these powder, and optimum dose was added and stirred, and the slurry was prepared. 260 g quart of this slurry was made monolith support with a diameter [of 103mm] x die length of 155mm as solid content, and desiccation of 120 degree-Cx 2 hours and baking of 500 degree-Cx 2 hours were performed. Next, after dipping this monolith support by which the coat was carried out in the dinitrodiammine platinum nitric-acid water solution of 3gPt considerable amount, and the water solution which dissolved the nitric-acid rhodium of a 0.65gRh considerable amount in 2000 cc ion exchange water and stirring for 2 hours, desiccation of 120 degree-Cx 2 hours and baking of 300 degree-Cx 1 hour were performed.

[0043] Next, 0.26 mols barium acetate and a 0.13-mol acetic-acid lithium were supported by the sinking-in method to the monolith support with which this Pt and Rh were supported, finally it calcinated at 500 degrees C to it, and the 3rd catalyst was acquired to it. The 1st acquired catalyst has been arranged to the exhaust manifold, the 2nd catalyst and the 3rd catalyst have been arranged on the lower stream of a river, it carried out like drawing 2 , and the exhaust gas purge of this invention was constituted.

[0044] The powder of perovskite mold multiple oxide $\text{La}_{0.7}\text{K}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ was obtained like the example 5 except having replaced with $\text{Sm}(\text{NO}_3)$ of 6780g of examples $3.6\text{H}_2\text{O}$, and having used 760g $\text{La}(\text{NO}_3)3.6\text{H}_2\text{O}$. The exhaust gas purge of this invention was constituted combining the 2nd catalyst and the 3rd catalyst which prepared the 1st catalyst like the example 5 and were prepared like the example 5 except having used 500g of this powder.

[0045] The powder of perovskite mold multiple oxide $\text{Nd}_{0.7}\text{K}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ was obtained like the example 5 except having replaced with $\text{Sm}(\text{NO}_3)$ of 7780g of examples $3.6\text{H}_2\text{O}$, and having used 770g $\text{Nd}(\text{NO}_3)3.6\text{H}_2\text{O}$. The exhaust gas purge of this invention was constituted combining the 2nd catalyst and the 3rd catalyst which prepared the 1st catalyst like the example 5 and were prepared like the example 5 except having used 500g of this powder.

[0046] The powder of perovskite mold multiple oxide $\text{Nd}_{0.7}\text{Rb}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ was obtained like the example 7 except having replaced with KNO_3 of 876g of examples, and having used 111g RbNO_3 . The exhaust gas purge of this invention was constituted combining the 2nd catalyst and the 3rd catalyst which prepared the 1st catalyst like the example 5 and were prepared like the example 5 except having used 500g of this powder.

[0047] The example of comparison 2 1st catalyst was not used, but the exhaust gas purge for a comparison was constituted combining the 2nd catalyst and the 3rd catalyst which were prepared like the example 5.

[0048] – The NO_x purification engine performance was evaluated about each of the exhaust gas purge of the examples 1–4 constituted like drawing 1 by the lower stream of a river of the evaluation-engine combustion chamber of the exhaust gas purification engine performance, and the example 1 of a comparison, and the

exhaust gas purge of the examples 5-8 constituted like drawing 2, and the example 2 of a comparison. The engine was used as the direct injection lean-burn engine with a displacement of 2000 cc in a cylinder (D-4 engine) by the serial 4-cylinder. It is made for the 1st catalyst inlet gas temperature to become 700 degrees C or 800 degrees C by having set the rotational frequency of this engine to 4500 - 5000rpm, and the NOx concentration (rate of NOx purification) in the gas of the 2nd catalyst outlet (examples 1-4 and example 1 of a comparison) to the NOx concentration in combustion chamber outlet gas or the 3rd catalyst outlet (examples 5-8 and example 2 of a comparison) estimated the catalyst engine performance.

[0049] This catalyst engine performance was evaluated after the first stage after catalyst manufacture, and the engine durability of 750 degree-Cx 50 hours. This evaluation result is combined with the summary of the configuration of an exhaust gas purge, and is shown in Table 1 and Table 2. This evaluation result shows that the exhaust gas purge by the configuration of this invention equipped with the catalyst of Pt support perovskite mold multiple oxide shows the rate of NO purification notably higher than the exhaust gas purge equipped with the catalyst of Pd support gamma-alumina of the example of a comparison.

[0050] Moreover, the examples 1-4 which supported the catalyst of Pt support perovskite mold multiple oxide and the catalyst of Pd support gamma-alumina to one monolith support, and the examples 5-8 which supported these catalysts to separate monolith support, and have arranged the catalyst of Pt support perovskite mold multiple oxide to the exhaust manifold show the equivalent rate of NOx purification.

[0051] RbNO [of 976.8g of examples / a Nd(NO3) 3.6H2O and 11.1g RbNO 3 and 50.4g] Mn(NO3) 2.6H2O, And after dissolving and stirring the titania sol containing 6g of solid content at 300 cc ion exchange water, Moisture was evaporated, baking of 850 degree-Cx 1 hour was performed after desiccation of 120 degree-Cx 2 hours, and temporary quenching of 480 degree-Cx 1 hour, and the powder of perovskite mold multiple oxide Nd0.7Rb0.3Mn0.7Ti 0.3O3 was obtained.

[0052] After having made 300 cc ion exchange water distribute 50g of this obtained multiple oxide powder, stirring and adding a dinitrodiammine platinum nitric-acid water solution by 2gPt considerable amount, moisture was evaporated, desiccation of 120 degree-Cx 2 hours and baking of 500 degree-Cx 1 hour were performed, Pt was supported on this multiple oxide, and the catalyst A of this invention was acquired.

[0053] The powder of perovskite mold multiple oxide Nd0.5Rb0.5Mn0.7Ti 0.3O3 was obtained like the example 9 using the titania sol containing Mn(NO3) 2.6H2O and 6g of solid content of Nd(NO3) 3.6H2O and 18.5 g of RbNO3 and 50.4 g. [of a 1054.9 g example] Subsequently, like the example 9, 2g Pt was supported to 50g of this obtained multiple oxide powder, and the catalyst B of this invention was acquired to it.

[0054] The powder of perovskite mold multiple oxide Sm0.7Rb0.3Mn0.7Ti 0.3O3 was obtained like the example 9 using the titania sol containing Mn(NO3) 2.6H2O and 6g of solid content of Sm(NO3) 3.6H2O and 11.1 g of RbNO3 and 50.4 g. [of a 1177.8 g example] Subsequently, like the example 9, 2g Pt was supported to 50g of this obtained multiple oxide powder, and the catalyst C of this invention was acquired to it.

[0055] The powder of perovskite mold multiple oxide La0.7Rb0.3Mn0.7Ti 0.3O3 was obtained like the example 9 using the titania sol containing Mn(NO3) 2.6H2O and 6g of solid content of La(NO3) 3.6H2O and 11.1 g of RbNO3 and 50.4 g. [of a 1275.8 g example] Subsequently, like the example 9, 2g Pt was supported to 50g of this obtained multiple oxide powder, and the catalyst D of this invention was acquired to it.

[0056] The powder of perovskite mold multiple oxide Nd0.7K0.3Mn0.7Ti 0.3O3 was obtained like the example 9 using the titania sol containing Nd(NO3) 3.6H2O, Mn(NO3) 2.6H2O with a KNO [3 and 50.4g] of 7.6g, and 6g of solid content of 376.8g of examples of a comparison. Subsequently, like the example 9, 2g Pt was supported to 50g of this obtained multiple oxide powder, and the catalyst D of the example of a comparison was acquired to it.

[0057] After having made 300 cc ion exchange water distribute gamma-alumina of 450g of examples of a comparison, having stirred, adding by 1gPt considerable amount and stirring a dinitrodiammine platinum nitric-acid water solution for 1 hour, it filters and dries, baking of 300 degree-Cx 1 hour is performed, and Pt could be supported on gamma-alumina. After heating and carrying out evaporation to dryness of this Pt support gamma-alumina, having distributed the solution made to dissolve 7.4g potassium acetate in 500 cc ion exchange water, and stirring, baking of 500 degree-Cx 2 hours was performed, and the catalyst F of the example of a comparison was acquired.

[0058] - Evaluation of the NOx purification engine performance - Each acquired catalyst was pressed and it was made the pellet which has size with a diameter of 0.5-1.7mm by subsequently grinding. Putting 2g of each [these] pellet catalyst to the ambient atmosphere which changes a rich model gas ambient atmosphere to following Lean for for [every] 2 minutes, respectively, the NOx purification engine performance was measured under lean atmosphere, and it asked for the rate of NOx purification by the following formula.

[0059] Rich-gas presentation: 2+0.3% O2 of 500ppmNO+2000ppmHC+0.6%CO+10%COs+5%H2O (remainder: N2)
Lean-gas presentation: 2+6.5% O2 of 500ppmNO+2000ppmHC+0.1%CO+10%COs+5%H2O (remainder: N2)

The rate of NOx purification = [(close gas concentration - appearance gas concentration) / close gas concentration] x 100 ambient temperature considered as four kinds, 400 degrees C, 500 degrees C, 600 degrees C, and 700 degrees C, and the result of the rate of NOx purification in each temperature was shown in drawing 3.

[0060] - When the rate of NOx purification is compared between - catalyst A-F from a result, gamma-alumina understands that the rate of NOx purification in 600 degrees C and 700 degrees C is notably higher than the catalyst F which ****(ed) Pt and a potassium for catalyst A-E which supported Pt to the specific perovskite mold multiple oxide.

[0061] When the rate of NOx purification is compared between catalyst A-E, the perovskite mold multiple oxide which does not contain a rubidium understands that 600 degrees C and the rate of NOx purification which can be set 700 degrees C are quite higher than the catalyst E which supported Pt for catalyst A-D which supported Pt to the perovskite mold multiple oxide containing a rubidium. A rubidium with this comparatively unstable exists in stability in a perovskite mold multiple oxide, and it is thought that it contributes to an elevated temperature and the high NOx occlusion engine performance.

[0062]

[Effect of the Invention] The temperature requirement which can purify NOx is expandable.

[0063]

[Table 1]

表 1. 排気ガス浄化装置の構成と評価結果

	排気ガス浄化装置の構成		NOx浄化率 (%)			
			700℃		800℃	
	第 1 触媒	第 2 触媒	初期	耐久後	初期	耐久後
実施例 1	Pt/Sn _{0.7} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃ +Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	66	30	59	38
実施例 2	Pt/La _{0.7} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃ +Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	62	28	58	32
実施例 3	Pt/Nd _{0.7} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃ +Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	68	32	62	46
実施例 4	Pt/Nd _{0.7} Rb _{0.3} Mn _{0.7} Ti _{0.3} O ₃ +Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	74	35	68	45
比較例 1	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	42	13	23	9

[0064]

[Table 2]

表 2. 排気ガス浄化装置の構成と評価結果

	排気ガス浄化装置の構成			NOx浄化率 (%)			
				700℃		800℃	
	第 1 触媒	第 2 触媒	第 3 触媒	初期	耐久後	初期	耐久後
実施例 5	Pt/Sn _{0.7} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	57	22	66	39
実施例 6	Pt/La _{0.7} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	56	24	64	38
実施例 7	Pt/Nd _{0.7} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	62	26	68	46
実施例 8	Pt/Nd _{0.7} Rb _{0.3} Mn _{0.7} Ti _{0.3} O ₃	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	68	28	72	47
比較例 2	Pd/Al ₂ O ₃	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	42	13	23	9

[Translation done.]

* NOTICES *

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- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram which illustrates the configuration of the exhaust gas purge of this invention.

[Drawing 2] It is the schematic diagram which illustrates the configuration of another mode of the exhaust gas purge of this invention.

[Drawing 3] It is the graph which compared the rate of NOx purification of various kinds of perovskite mold multiple oxide catalysts.

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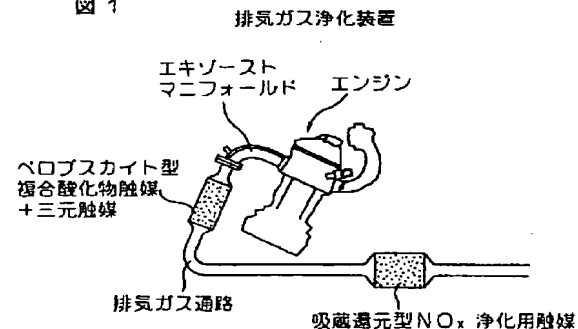
(54) 【発明の名称】 内燃機関の排気ガス浄化装置及び排気ガス浄化用触媒

(57) 【要約】

【課題】 NO_xを浄化可能な温度範囲が拡大された排気ガス浄化装置を提供する。

【解決手段】 リーンバーンエンジンの排気ガス通路の上流側に、少なくとも2種の金属を含むペロブスカイト型複合酸化物に貴金属を担持した触媒が配置され、前記触媒の下流側にNO_xを浄化する触媒が配置されたことを特徴とする排気ガス浄化装置である。好ましくは、ペロブスカイト型複合酸化物は、化学式： $A_{1-x}A'_xM_{1-y}Ti_yO_3$ (Aは、La、Nd、Sm、及びGdの少なくとも1種、A'は、K、Rb、及びCsの少なくとも1種、Mは、Mn、Co、Fe、及びNiの少なくとも1種、 $0 < x < 1$ 、 $0 < y < 1$) で表され、より好ましくは、A'はRbである。

図 1



【特許請求の範囲】

【請求項1】 リーンバーンエンジンの排気ガス通路の上流側に、少なくとも2種の金属を含むペロブスカイト型複合酸化物に貴金属を担持した触媒が配置され、前記触媒の下流側にNO_xを浄化する触媒が配置されたことを特徴とする排気ガス浄化装置。

【請求項2】 リーンバーンエンジンの排気ガス通路の上流側に、化学式： $A_{1-x}A'_yM_{1-y}Ti_xO_3$ （Aは、La、Nd、Sm、及びGdの少なくとも1種、A'は、K、Rb、及びCsの少なくとも1種、Mは、Mn、Co、Fe、及びNiの少なくとも1種、 $0 < x < 1$ 、 $0 < y < 1$ ）で表されるペロブスカイト型複合酸化物に貴金属を担持した触媒が配置され、前記触媒の下流側にNO_xを浄化する触媒が配置されたことを特徴とする排気ガス浄化装置。

【請求項3】 化学式： $A_{1-x}Rb_yM_{1-y}Ti_xO_3$ （Aは、La、Nd、Sm、及びGdの少なくとも1種、Mは、Mn、Co、Fe、及びNiの少なくとも1種、 $0 < x < 1$ 、 $0 < y < 1$ ）で表されるペロブスカイト型複合酸化物に貴金属が担持されたことを特徴とする排気ガス浄化用触媒。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、自動車用エンジン等の内燃機関から排出される排気ガスを浄化するための装置に関し、より詳しくは、NO_xを浄化可能な温度範囲が拡大された排気ガス浄化装置に関する。

【0002】

【従来の技術】近年、環境保護のため、自動車用エンジン等の内燃機関から排出される二酸化炭素（CO₂）の総量を抑えること、及び窒素酸化物（NO_x）の発生量を抑えることが世界的な課題となっている。この対応策として、燃費向上の目的でリーンバーンエンジンが開発され、その排気ガスを浄化する目的で、従来の三元触媒にリーン雰囲気中でNO_xを吸蔵する機能を付加させた吸蔵還元型NO_x浄化用触媒が開発され、上記課題に対して一定の成功を収めている。

【0003】このリーンバーンエンジンは、燃料を、常時は空燃比（A/F）がリーン（空気過剰）の条件下で燃焼させ、一時的にストイキ（理論空燃比）〜リッチ（燃料過剰）の条件下で燃焼させる。排気ガス中の炭化水素（HC）や一酸化炭素（CO）は、リーン側で酸化性雰囲気と触媒の作用により効率的に燃焼除去され、一方、NO_xはリーン側では吸蔵材に捕捉され、それが一時的なストイキ〜リッチ条件下において放出され、その一時的な還元性雰囲気と触媒の作用により還元浄化される。

【0004】従来、この吸蔵還元型NO_x浄化用触媒のNO_x吸蔵材には、アルカリ金属又はアルカリ土類金属等が使用され、白金等の触媒成分とNO_x吸蔵材の塩

を、γ-アルミナ等の担体に担持して排気ガス浄化用触媒が構成される。こうした排気ガス浄化用触媒は、例えば、特開平9-248458号公報、特開平10-33984号公報、特開平10-128114号公報に記載されている。

【0005】一方、特定のペロブスカイト型複合酸化物はNO_xをN₂とO₂に分解する作用を有することが知られており、例えば、特開平5-261289号公報、特開平5-245372号公報、特開平6-315634号公報に、特定のペロブスカイト型複合酸化物を担体に担持したNO_x接触還元用触媒が記載されている。

【0006】

【発明が解決しようとする課題】しかしながら、アルカリ金属又はアルカリ土類金属等を担持した吸蔵還元型NO_x浄化用触媒では、約500℃を上回る触媒温度におけるNO_x浄化性能を高める必要があった。また、エンジン始動時のような排気ガス温度が低い条件下でのNO_x浄化性能を高める必要もあった。

【0007】また、かかる吸蔵還元によってNO_xを浄化する方式では、触媒に導入するNO_xを還元するための一時的なストイキ〜リッチ条件下での燃焼を必要とするが、このような燃焼は、燃料の一部を使用し、燃費を一部犠牲にすることで発生させる。このため、さらに燃費を向上させるためには、一時的なストイキ〜リッチ条件下での燃焼の頻度を出来るだけ少なくすることが望まれる。一方、従来のペロブスカイト型複合酸化物を含む触媒は、自動車用エンジン等の内燃機関から排出される排気ガスの浄化に使用するためには、NO_x浄化性能を高める必要があった。

【0008】したがって、本発明は、とりわけ、NO_xを浄化可能な温度範囲を従来よりも拡大させることができる排気ガス浄化装置を提供することを目的とする。

【0009】

【課題を解決するための手段】上記目的は、リーンバーンエンジンの排気ガス通路の上流側に、少なくとも2種の金属を含むペロブスカイト型複合酸化物に貴金属を担持した触媒が配置され、この触媒の下流側にNO_xを浄化する触媒が配置されたことを特徴とする排気ガス浄化装置によって達成される。

【0010】即ち、本発明は、特定のペロブスカイト型複合酸化物の上に、白金等の貴金属が直接担持されてなる触媒（以下、「ペロブスカイト型複合酸化物触媒」と称する。）を、排気ガス通路の上流側に配置し、その下流側にNO_x浄化用触媒が配置された排気ガス浄化装置である。かかる構成の排気ガス浄化装置によって上記の目的が達成される理由は、以下のように考えられる。

【0011】少なくとも2種の金属元素を含むペロブスカイト型複合酸化物は、一般に、含まれる金属元素の原子半径の相違によって結晶にひずみが生じおり、この結晶ひずみがNO_xに何らかの活性作用を及ぼし、かかる

活性作用と白金等の触媒成分の作用が相乗的に作用するものと考えられる。そして、この相乗的作用は、白金等の触媒成分がペロブスカイト型複合酸化物の上に直接担持されることで顕著になり、NO_xをN₂とO₂に分解する作用が高められるものと考えられる。

【0012】ここで、特定のペロブスカイト型複合酸化物触媒は、排気ガス温度が1000℃を上回る条件下でも十分な耐久性を有し、NO_xを分解浄化する作用を維持できることが明らかになった。このため、こうしたペロブスカイト型複合酸化物触媒は、通常のNO_x浄化用触媒に付加して、上流側のエンジン燃焼室に近い位置に配置し、温度が高い条件下で排気ガス中のNO_xを浄化する触媒として使用されることができる。それにより、NO_xを浄化可能な上限温度が高められるのみならず、下流側のNO_x浄化用触媒がNO_xを浄化する負荷が軽減されることで、排気ガス浄化装置の全体としてNO_x浄化性能を高めることができる。

【0013】また、この下流側のNO_x浄化用触媒が吸蔵還元型NO_x浄化用触媒であれば、吸蔵されるNO_x量が低減されることから、一時的なストイキ〜リッチ条件下での燃焼の頻度を少なくすることができ、燃費の向上をもたらすことができる。また、上流側のペロブスカイト型複合酸化物触媒は、エンジン燃焼室に近い位置に配置されることで、下流側のNO_x浄化用触媒と比較して、エンジン始動時に触媒温度が迅速に高くなり、このため、NO_xをより早期に浄化可能とすることもできる。

【0014】また、本発明の排気ガス浄化装置は、これらのペロブスカイト型複合酸化物触媒とNO_x浄化用触媒に加えて、γ-アルミナのような金属酸化物担体に貴金属等を担持した三元触媒を備えることができる。これにより、HCとCOについてもより高い浄化性能を得ることができ、さらに、ペロブスカイト型複合酸化物触媒と三元触媒を共存させれば、三元触媒の触媒活性によって触媒床温度が上昇することにより、ペロブスカイト型複合酸化物触媒のNO_x浄化性能が向上し、下流側のNO_x浄化用触媒のNO_xを浄化する負荷が一層軽減される。

【0015】

【発明の実施の形態】本発明の排気ガス浄化装置は、リーンバーンエンジンの排気ガス通路の上流側に、少なくとも2種の金属を含むペロブスカイト型複合酸化物に貴金属を担持したペロブスカイト型複合酸化物触媒が配置され、この触媒の下流側にNO_x浄化用触媒が配置されて構成される。このリーンバーンエンジンには、気筒内全体としてはリーンな混合気を燃焼させて成層燃焼を実現する筒内噴射式火花点火内燃機関等が例示され、また、ディーゼル式内燃機関も含まれる。これらの内燃機関は、リーン条件下で燃料を燃焼させることからNO_xが比較的多量に発生し、NO_xの浄化が必要となる。

【0016】ペロブスカイト型複合酸化物は、少なくとも2種の金属元素を含んでなる。ここで、金属元素は、s-ブロック金属元素、d-ブロック金属元素、p-ブロック金属元素、f-ブロック金属元素から任意に選択することができ、具体的には、ナトリウム(Na)、カリウム(K)、ルビジウム(Rb)、セシウム(Cs)、カルシウム(Ca)、バリウム(Ba)、ストロンチウム(Sr)、ランタン(La)、イットリウム(Y)、セリウム(Ce)、プラセオジウム(Pr)、ネオジム(Nd)、サマリウム(Sm)、ユウロピウム(Eu)、ガドリニウム(Gd)、チタン(Ti)、錫(Sn)、ジルコニウム(Zr)、マンガン(Mn)、鉄(Fe)、コバルト(Co)、ニッケル(Ni)、クロム(Cr)、ニオブ(Nb)、銅(Cu)、バナジウム(V)、モリブデン(Mo)、タングステン(W)、亜鉛(Zn)、及びタンタル(Ta)等であることができる。

【0017】好ましい態様において、ペロブスカイト型複合酸化物は、A_{1-x}A'_xM_{1-y}Ti_yO₃ (Aは、La、Nd、Sm、及びGdの少なくとも1種、A'は、K、Rb、及びCsの少なくとも1種、Mは、Mn、Co、Fe、及びNiの少なくとも1種)の化学式を有するTiを含む特定のペロブスカイト型複合酸化物であり、0<x<1であり、より好ましくは0.05<x<0.45、さらに好ましくは0.2<x<0.4であり、0<y<1であり、より好ましくは0.05<y<0.45、さらに好ましくは0.2<y<0.4である。

【0018】より好ましくは、ペロブスカイト型複合酸化物は、A_{1-x}Rb_xM_{1-y}Ti_yO₃ (Aは、La、Nd、Sm、及びGdの少なくとも1種、Mは、Mn、Co、Fe、及びNiの少なくとも1種)の化学式を有するRbとTiを含む特定のペロブスカイト型複合酸化物であり、0<x<1であり、より好ましくは0.05<x<0.45、さらに好ましくは0.2<x<0.4であり、0<y<1であり、より好ましくは0.05<y<0.45、さらに好ましくは0.2<y<0.4である。

【0019】こうした特定のペロブスカイト型複合酸化物に貴金属が担持されたペロブスカイト型複合酸化物触媒は、高温下でより高いNO_x浄化性能を提供することができ、また、耐久性にも優れることが見出されている。この理由は、必ずしも明らかではないが、以下のよう推察される。

【0020】上記のような化学式を有するペロブスカイト型複合酸化物は、その結晶格子の一部を特定の元素によって置換されるため、上述の原子半径の相違による結晶のひずみに加えて、結晶構造がより不安定になり、酸素原子が価数変化を生じ、酸素を吸放出することができるためと考えられる。また、かかる構造のペロブスカイト型複合酸化物では、Bサイトの元素が酸化還元作用を奏することができ、この酸化還元作用は、とりわけ、B

サイトの元素の一部がチタンで置換されたときに顕著になるものと推定される。

【0021】また、次のことが理由として考えられる。従来のアルカリ金属又はアルカリ土類金属が担持された吸蔵還元型NO_x浄化用触媒においては、アルカリ金属又はアルカリ土類金属は、リーン条件下では硝酸塩に、リッチ条件下では炭酸塩に変化するものと考えられる。これらの塩は、約500℃を上回る温度では分解が生じ、このため、高温でのNO_x吸蔵性能が低下するものと考えられる。

【0022】これに対して、上記のペロブスカイト型複合酸化物は、複合効果により高温下でも安定化される一方で、高温下では、Aサイトのカリウム、ルビジウム、又はセシウムの少なくとも一部がペロブスカイト型複合酸化物から遊離することができ、残存する負イオンがNO_xに対して塩基点として作用し、負イオン化されたNO_xを正イオンのカリウム、ルビジウム、又はセシウムが捕獲するものと推定される。また、ルビジウムは、中でも不安定な性質を有し、その性質がNO_xのこうした捕獲を効果的にもたらすためと推定される。

【0023】このように、上記の特定のペロブスカイト型複合酸化物は、その酸素吸放出等の作用が貴金属の触媒作用と相乗的に作用することができ、さらに、高温下でNO_x吸蔵材として機能することができ、それによって、高温下での高いNO_x浄化性能を提供するものと推定される。

【0024】このようなペロブスカイト型複合酸化物の調製は、例えば、含まれる元素の硝酸塩、酢酸塩、塩化物等の粉末を所定の割合で混合した後、あるいは、水溶液にして混合・乾燥した後、空気中で400～1000

℃に加熱することにより行うことができる。
【0025】このようなペロブスカイト型複合酸化物に、白金(Pt)、パラジウム(Pd)、ロジウム(Rh)、金(Au)、銀(Ag)、及びイリジウム(Ir)の少なくとも1種から選択された貴金属が担持されて、ペロブスカイト型複合酸化物触媒が調製される。この担持は、担体上に金属粒子を担持させることができる任意の方法から選択された、例えば、析出法、吸着法、イオン交換法、還元析出法、蒸発乾固法等によって行うことができる。

【0026】好ましくは、この貴金属は、ペロブスカイト型複合酸化物の質量100gを基準に、0.1～5g、より好ましくは0.3～4gの量で担持される。好ましくは、ペロブスカイト型複合酸化物を粉碎等によって0.05～20μmの粒径に調整した後に、貴金属を担持する。貴金属をペロブスカイト型複合酸化物の上により均一に分散させるためである。

【0027】ペロブスカイト型複合酸化物触媒の下流側に配置されるNO_x浄化用触媒は、NO_xを浄化することができる任意の触媒であることができ、例えば、アルカ

リ金属又はアルカリ土類金属等のNO_x吸蔵材と白金等の触媒成分が、γ-アルミナ等の担体に担持された吸蔵還元型NO_x浄化用触媒であることができる。また、このNO_x浄化用触媒は、塩基点や細孔によってNO_xを一時的又は長期的に吸着又は吸収するゼオライト、アルカリ物質、各種複合酸化物のような吸着材又は吸収材であることもできる。

【0028】また、本発明の排気ガス浄化装置は、これらのペロブスカイト型複合酸化物触媒とNO_x浄化用触媒に加えて、γ-アルミナのような金属酸化物担体に貴金属が担持された三元触媒を備えることができる。この三元触媒は、ペロブスカイト型複合酸化物触媒と共存して配置されることができ、あるいは、ペロブスカイト型複合酸化物触媒の下流側に配置されることができ

【0029】これらのペロブスカイト型複合酸化物触媒、NO_x浄化用触媒、三元触媒は、ハニカム形状の通常のモノリス担体にウォッシュコート等によりコートすることで、排気ガス通路を有する触媒とすることができるが、排気管の内壁に直接コートすることでも、本発明の排気ガス浄化装置を構成することができる。

【0030】図1～2は、本発明の排気ガス浄化装置の構成を模式的に例示するものであり、図1は、エンジン燃焼室の下流の排気管にペロブスカイト型複合酸化物触媒と三元触媒と一緒に配置され、その下流に吸蔵還元型NO_x浄化用触媒が配置された例である。図2は、エンジン燃焼室出口のエキゾーストマニホールドにペロブスカイト型複合酸化物触媒が配置され、その下流に三元触媒と吸蔵還元型NO_x浄化用触媒が配置された例である。以下、実施例によって本発明をより具体的に説明する。

【0031】

【実施例】実施例1～4は、図1の構成の排気ガス浄化装置を例証し、実施例5～8は、図2の構成の排気ガス浄化装置を例証し、実施例9～12は、高温でのNO_x浄化性能に優れるペロブスカイト型複合酸化物触媒を例証する。

【0032】実施例1

ペロブスカイト型複合酸化物触媒と三元触媒からなる第1触媒を以下のようにして調製した。780gのSm(NO₃)₃・6H₂O、76gのKNO₃、504gのMn(NO₃)₂・6H₂O、及び固形分60gを含むチタニアゾルを3000ccのイオン交換水に溶解・攪拌した後、水分を蒸発させ、120℃×2時間の乾燥と480℃×5時間の仮焼を行い、次いで850℃×10時間の焼成を行って、ペロブスカイト型複合酸化物Sm_{0.7}K_{0.3}Mn_{0.4}Ti_{0.3}O₃の粉末を得た。得られたこの複合酸化物粉末500gを2000ccのイオン交換水に分散させて攪拌し、ジニトロジアンミン白金硝酸水溶液を20gPt相当量で添加した後、水分を蒸発させ、120℃×2時間の乾燥と500℃×2時間の焼成を行って、Pt担持ペロブスカイト型複合酸化物粉末を得た。

【0033】次に、このPt担持ペロブスカイト型複合酸化物粉末に、250gのγ-アルミナ粉末を混合し、総固形分を基準に固形分20質量%に相当するアルミナゾルと適量のイオン交換水を添加し、攪拌してスラリーを調製した。このスラリーを、直径93mm×長さ100mmのモノリス担体に、固形分として210gコートし、120℃×2時間の乾燥と500℃×2時間の焼成を行った後、3.5gPd相当量の硝酸パラジウム水溶液を用い、イオン交換法によりパラジウムをさらに担持して第1触媒を得た。

【0034】吸蔵還元型NO_x浄化用触媒からなる第2触媒を以下のようにして調製した。300gのγ-アルミナ粉末と300gのチタニア粉末に、これらの粉末との総固形分を基準に固形分30質量%に相当するアルミナゾルと適量のイオン交換水を添加し、攪拌してスラリーを調製した。このスラリーを、直径103mm×長さ155mmのモノリス担体に、固形分として260gコートし、120℃×2時間の乾燥と500℃×2時間の焼成を行った。

【0035】次に、3gPt相当量のジニトロジアンミン白金硝酸水溶液と0.65gRh相当量の硝酸ロジウムを2000ccのイオン交換水に溶解した水溶液に、このコートされたモノリス担体を浸し、2時間攪拌した後、120℃×2時間の乾燥と300℃×1時間の焼成を行った。次に、このPtとRhが担持されたモノリス担体に、0.26モルの酢酸バリウムと0.13モルの酢酸リチウムを含浸法によって担持し、最終的に500℃で焼成して第2触媒を得た。得られた第1触媒と第2触媒を、図1のようにエンジン燃焼室の下流に配置し、本発明の排気ガス浄化装置を構成した。

【0036】実施例2

780gのSm(NO₃)₃・6H₂Oに代えて760gのLa(NO₃)₃・6H₂Oを用いた以外は、実施例1と同様にして、ペロブスカイト型複合酸化物La_{0.7}K_{0.3}Mn_{0.7}Ti_{0.3}O₃の粉末を得た。この粉末500gを用いた以外は実施例1と同様にして第1触媒を調製し、実施例1と同様にして調製した第2触媒と組み合わせて、本発明の排気ガス浄化装置を構成した。

【0037】実施例3

780gのSm(NO₃)₃・6H₂Oに代えて770gのNd(NO₃)₃・6H₂Oを用いた以外は、実施例1と同様にして、ペロブスカイト型複合酸化物Nd_{0.7}K_{0.3}Mn_{0.7}Ti_{0.3}O₃の粉末を得た。この粉末500gを用いた以外は実施例1と同様にして第1触媒を調製し、実施例1と同様にして調製した第2触媒と組み合わせて、本発明の排気ガス浄化装置を構成した。

【0038】実施例4

76gのKNO₃に代えて111gのRbNO₃を用いた以外は、実施例3と同様にして、ペロブスカイト型複合酸化物Nd_{0.7}Rb_{0.3}Mn_{0.7}Ti_{0.3}O₃の粉末を得

た。この粉末500gを用いた以外は実施例1と同様にして第1触媒を調製し、実施例1と同様にして調製した第2触媒と組み合わせて、本発明の排気ガス浄化装置を構成した。

【0039】比較例1

ペロブスカイト型複合酸化物の粉末を用いない以外は、実施例1と同様にして、直径93mm×長さ100mmのモノリス担体に、70gのγ-アルミナをコートし、次に、3.5gPd相当量の硝酸パラジウム水溶液を用いてパラジウムをさらに担持し、第1触媒を調製した。この第1触媒と、実施例1と同様にして調製した第2触媒と組み合わせて、比較用の排気ガス浄化装置を構成した。

【0040】実施例5

ペロブスカイト型複合酸化物触媒からなる第1触媒を以下のようにして調製した。実施例1と同様にして、ペロブスカイト型複合酸化物Sm_{0.7}K_{0.3}Mn_{0.7}Ti_{0.3}O₃の粉末を作成し、この粉末500gに、実施例1と同様にして、20gのPtを担持した。得られたPt担持ペロブスカイト型複合酸化物の粉末に、総固形分を基準に固形分30質量%に相当するアルミナゾルと適量のイオン交換水を添加し、攪拌してスラリーを調製した。このスラリーを、直径80mm×長さ95mmのモノリス担体に、固形分として100gコートし、120℃×2時間の乾燥と500℃×1時間の焼成を行い、第1触媒を得た。

【0041】三元触媒からなる第2触媒を以下のようにして調製した。γ-アルミナ粉末に、この粉末との総固形分を基準に固形分20質量%に相当するアルミナゾルと適量のイオン交換水を添加し、攪拌してスラリーを調製した。このスラリーを、直径93mm×長さ100mmのモノリス担体に、固形分として210gコートし、120℃×2時間の乾燥と500℃×2時間の焼成を行った後、3.5gPd相当量の硝酸パラジウム水溶液を用いて、イオン交換法によりパラジウムを担持し、第2触媒を得た。

【0042】吸蔵還元型NO_x浄化用触媒からなる第3触媒を以下のようにして調製した。300gのγ-アルミナ粉末と300gのチタニア粉末に、これらの粉末との総固形分を基準に固形分30質量%に相当するアルミナゾルと適量のイオン交換水を添加し、攪拌してスラリーを調製した。このスラリーを、直径103mm×長さ155mmのモノリス担体に、固形分として260gコートし、120℃×2時間の乾燥と500℃×2時間の焼成を行った。次に、3gPt相当量のジニトロジアンミン白金硝酸水溶液と0.65gRh相当量の硝酸ロジウムを2000ccのイオン交換水に溶解した水溶液に、このコートされたモノリス担体を浸し、2時間攪拌した後、120℃×2時間の乾燥と300℃×1時間の焼成を行った。

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【0043】次に、このPtとRhが担持されたモノリス担体に、0.26モルの酢酸バリウムと0.13モルの酢酸リチウムを含む法によって担持し、最終的に500℃で焼成して第3触媒を得た。得られた第1触媒をエキゾーストマニホルドに配置し、その下流に第2触媒と第3触媒を配置し、図2のようにして、本発明の排気ガス浄化装置を構成した。

【0044】実施例6

780gの $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ に代えて760gの $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ を用いた以外は、実施例5と同様にして、ペロブスカイト型複合酸化物 $\text{La}_{0.7}\text{K}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ の粉末を得た。この粉末500gを用いた以外は実施例5と同様にして第1触媒を調製し、実施例5と同様にして調製した第2触媒及び第3触媒と組み合わせて、本発明の排気ガス浄化装置を構成した。

【0045】実施例7

780gの $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ に代えて770gの $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ を用いた以外は、実施例5と同様にして、ペロブスカイト型複合酸化物 $\text{Nd}_{0.7}\text{K}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ の粉末を得た。この粉末500gを用いた以外は実施例5と同様にして第1触媒を調製し、実施例5と同様にして調製した第2触媒及び第3触媒と組み合わせて、本発明の排気ガス浄化装置を構成した。

【0046】実施例8

76gの KNO_3 に代えて111gの RbNO_3 を用いた以外は、実施例7と同様にして、ペロブスカイト型複合酸化物 $\text{Nd}_{0.7}\text{Rb}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ の粉末を得た。この粉末500gを用いた以外は実施例5と同様にして第1触媒を調製し、実施例5と同様にして調製した第2触媒及び第3触媒と組み合わせて、本発明の排気ガス浄化装置を構成した。

【0047】比較例2

第1触媒を使用せず、実施例5と同様にして調製した第2触媒と第3触媒を組み合わせて、比較用の排気ガス浄化装置を構成した。

【0048】-排気ガス浄化性能の評価-

エンジン燃焼室の下流に、図1のように構成された実施例1～4と比較例1の排気ガス浄化装置、及び図2のように構成された実施例5～8と比較例2の排気ガス浄化装置の各々について、 NO_x 浄化性能を評価した。エンジンは、直列4気筒で排気量2000ccの筒内直噴希薄燃焼エンジン（D-4エンジン）とした。このエンジンの回転数を4500～5000rpmとして、第1触媒入口ガス温度が700℃又は800℃となるようにし、燃焼室出口ガス中の NO_x 濃度に対する第2触媒出口（実施例1～4と比較例1）又は第3触媒出口（実施例5～8と比較例2）のガス中の NO_x 濃度（ NO_x 浄化率）で触媒性能を評価した。

【0049】この触媒性能は、触媒製造後の初期と750℃×50時間のエンジン耐久後で評価した。この評価

結果を、排気ガス浄化装置の構成の概要と併せて表1と表2に示す。この評価結果から、Pt担持ペロブスカイト型複合酸化物の触媒を備えた本発明の構成による排気ガス浄化装置は、比較例のPd担持γ-アルミナの触媒を備えた排気ガス浄化装置よりも顕著に高い NO 浄化率を示すことがわかる。

【0050】また、Pt担持ペロブスカイト型複合酸化物の触媒とPd担持γ-アルミナの触媒を1つのモノリス担体に担持した実施例1～4と、これらの触媒を別々のモノリス担体に担持して、Pt担持ペロブスカイト型複合酸化物の触媒をエキゾーストマニホルドに配置した実施例5～8は、同等な NO_x 浄化率を示している。

【0051】実施例9

76.8gの $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、11.1gの RbNO_3 、50.4gの $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、及び固形分6gを含むチタニアゾルを300ccのイオン交換水に溶解・攪拌した後、水分を蒸発させ、120℃×2時間の乾燥と480℃×1時間の仮焼の後、850℃×1時間の焼成を行って、ペロブスカイト型複合酸化物 $\text{Nd}_{0.7}\text{Rb}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ の粉末を得た。

【0052】得られたこの複合酸化物粉末50gを300ccのイオン交換水に分散させて攪拌し、ジニトロロジアンミン白金硝酸水溶液を2gPt相当量で添加した後、水分を蒸発させ、120℃×2時間の乾燥と500℃×1時間の焼成を行ってPtをこの複合酸化物の上に担持し、本発明の触媒Aを得た。

【0053】実施例10

54.9gの $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、18.5gの RbNO_3 、50.4gの $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、及び固形分6gを含むチタニアゾルを用い、実施例9と同様にしてペロブスカイト型複合酸化物 $\text{Nd}_{0.7}\text{Rb}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ の粉末を得た。次いで、得られたこの複合酸化物粉末50gに、実施例9と同様にして、2gのPtを担持し、本発明の触媒Bを得た。

【0054】実施例11

77.8gの $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、11.1gの RbNO_3 、50.4gの $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、及び固形分6gを含むチタニアゾルを用い、実施例9と同様にしてペロブスカイト型複合酸化物 $\text{Sm}_{0.7}\text{Rb}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ の粉末を得た。次いで、得られたこの複合酸化物粉末50gに、実施例9と同様にして、2gのPtを担持し、本発明の触媒Cを得た。

【0055】実施例12

75.8gの $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、11.1gの RbNO_3 、50.4gの $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、及び固形分6gを含むチタニアゾルを用い、実施例9と同様にしてペロブスカイト型複合酸化物 $\text{La}_{0.7}\text{Rb}_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ の粉末を得た。次いで、得られたこの複合酸化物粉末50gに、実施例9と同様にして、2gのPtを担持し、本発明の触媒Dを得た。

【0056】比較例3

76.8gのNd(NO₃)₃・6H₂O、7.6gのKN O₃、50.4gのMn(NO₃)₂・6H₂O、及び固形分6gを含むチタニアゾルを用い、実施例9と同様にしてペロブスカイト型複合酸化物Nd_{0.7}K_{0.3}Mn_{0.7}Ti_{0.3}O₃の粉末を得た。次いで、得られたこの複合酸化物粉末50gに、実施例9と同様にして、2gのPtを担持し、比較例の触媒Dを得た。

【0057】比較例4

50gのγ-アルミナを300ccのイオン交換水に分散させて攪拌し、ジニトロジアンミン白金硝酸水溶液を1gPt相当量で添加し、1時間攪拌した後、濾過・乾燥し、300℃×1時間の焼成を行ってPtをγ-アルミナの上に担持し得た。このPt担持γ-アルミナを、500ccのイオン交換水に7.4gの酢酸カリウムを溶解させた溶液に分散させ、攪拌しながら加熱して蒸発乾固させた後、500℃×2時間の焼成を行って、比較例の触媒Fを得た。

【0058】-NOx浄化性能の評価-

得られた各触媒を圧縮成形し、次いで粉砕することにより直径0.5~1.7mmのサイズを有するペレットにした。これら各ペレット触媒の2gを、下記のリーンとリッチのモデルガス雰囲気それぞれ2分間毎に切り替える雰囲気中に曝しながら、リーン雰囲気下でNOx浄化性能を測定し、下記の式によってNOx浄化率を求めた。

【0059】リッチガス組成：

500ppmNO+2000ppmHC+0.6%CO
+10%CO₂+0.3%O₂+5%H₂O(残余：N₂)

＊リーンガス組成：

500ppmNO+2000ppmHC+0.1%CO
+10%CO₂+6.5%O₂+5%H₂O(残余：N₂)
NOx浄化率=[(入ガス濃度-出ガス濃度)÷入ガス濃度]×100

雰囲気温度は、400℃、500℃、600℃、及び700℃の4通りとし、各温度におけるNOx浄化率の結果を図3に示した。

【0060】-結果より-

触媒A~Fの間でNOx浄化率を比較すると、特定のペロブスカイト型複合酸化物にPtを担持した触媒A~Eは、γ-アルミナにPtとカリウムを担持した触媒Fよりも、600℃と700℃におけるNOx浄化率が顕著に高いことが分かる。

【0061】触媒A~Eの間でNOx浄化率を比較すると、ルビジウムを含むペロブスカイト型複合酸化物にPtを担持した触媒A~Dは、ルビジウムを含まないペロブスカイト型複合酸化物にPtを担持した触媒Eよりも、600℃と700℃におけるNOx浄化率がかなり高いことが分かる。このことは、比較的不安定なルビジウムが、ペロブスカイト型複合酸化物の中で安定に存在し、高温での高いNOx吸蔵性能に寄与するものと考えられる。

【0062】

【発明の効果】NOxを浄化可能な温度範囲が拡大できる。

【0063】

【表1】

表1. 排気ガス浄化装置の構成と評価結果

	排気ガス浄化装置の構成		NOx浄化率 (%)			
			700℃		800℃	
	第1触媒	第2触媒	初期	耐久後	初期	耐久後
実施例1	Pt/Sm _{0.7} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃ +Pd/Al ₂ O ₃	Pt/Ba/K/Li/(Al ₂ O ₃ +TiO ₂)	66	30	59	38
実施例2	Pt/La _{0.7} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃ +Pd/Al ₂ O ₃	Pt/Ba/K/Li/(Al ₂ O ₃ +TiO ₂)	62	28	58	32
実施例3	Pt/Nd _{0.7} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃ +Pd/Al ₂ O ₃	Pt/Ba/K/Li/(Al ₂ O ₃ +TiO ₂)	68	32	62	46
実施例4	Pt/Nd _{0.7} Rb _{0.3} Mn _{0.7} Ti _{0.3} O ₃ +Pd/Al ₂ O ₃	Pt/Ba/K/Li/(Al ₂ O ₃ +TiO ₂)	74	35	68	45
比較例1	Pd/Al ₂ O ₃	Pt/Ba/K/Li/(Al ₂ O ₃ +TiO ₂)	42	13	23	9

【0064】

【表2】

表2. 排気ガス浄化装置の構成と評価結果

	排気ガス浄化装置の構成			NO _x 浄化率 (%)			
				700℃		800℃	
	第1触媒	第2触媒	第3触媒	初期	耐久後	初期	耐久後
実施例5	Pt/Sn _{0.1} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	57	22	66	39
実施例6	Pt/La _{0.1} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	58	24	64	38
実施例7	Pt/Nd _{0.1} K _{0.3} Mn _{0.7} Ti _{0.3} O ₃	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	62	26	68	46
実施例8	Pt/Nd _{0.1} Rb _{0.3} Mn _{0.7} Ti _{0.3} O ₃	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	68	28	72	47
比較例2	Pd/Al ₂ O ₃	Pd/Al ₂ O ₃	Pt/Ba/K/Li/ (Al ₂ O ₃ +TiO ₂)	42	13	23	9

【図面の簡単な説明】

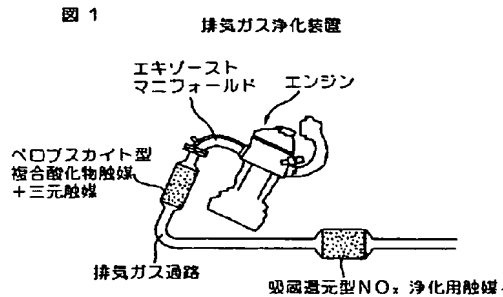
【図1】 本発明の排気ガス浄化装置の構成を例示する概略図である。

【図2】 本発明の排気ガス浄化装置の別な態様の構成を*20

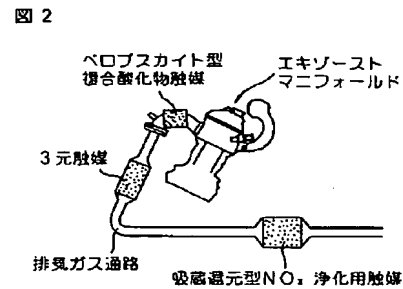
* 例示する概略図である。

【図3】 各種のペロブスカイト型複合酸化物触媒のNO_x浄化率を比較したグラフである。

【図1】



【図2】



【図3】

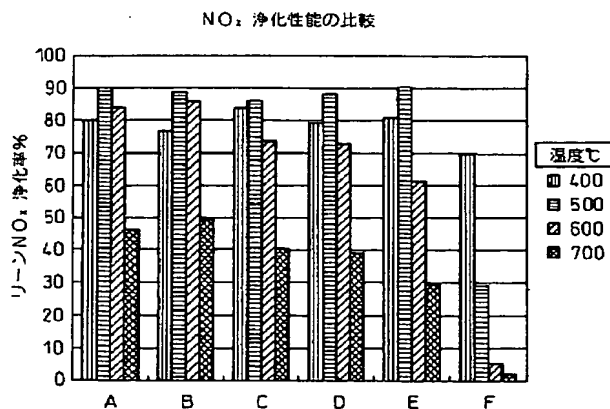


図3

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